Economics of new MTBE design

An MTBE process using sulfuric acid catalyst can be economical in locations where low cost isobutene and methanol are available

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METHYL TERTIARY BUTYL ETHER (MTBE) is produced industrially by catalytic reaction between methanol and isobutene. The catalyst that is widely used is an acidic ion exchange resin. This article explores design and economics when sulfuric acid is the catalyst.

The profitability of MTBE production depends mainly on the cost of butenes and methanol. Thus, our example shows MTBE made with a catalyst of sulfuric acid was profitable at a Saudi Arabian location, even though it was not profitable at a U.S. Gulf Coast location.

PROCESS DESIGN

The reaction of isobutene and methanol using sulfuric acid catalyst is carried out in a liquid phase. The reaction is exothermic and produces 10.2 kcal/mol of MTBE.

The process plant will produce 100,000 metric tons per year (tpy) or 2,320 barrels per calendar day (bpcd) with an onstream factor of 0.90 (or 328 days/yr). The mixed butenes feed is obtained from a source containing 45 wt% isobutene and 55 wt% other C_4 hydrocarbons. The required isobutene conversion is 98%. The MTBE product has a purity of 99 wt%. A flowsheet of the process is shown in Fig. 1. The process units consist of: two reactors, a settler, a water washing column, a methanol column and an MTBE column.

A summary of the design basis is given in Table 1. The MTBE production rate of 100,000 tpy and the stream factor of 0.90 are the usual values taken in economic studies. The C_4 feed composition is assumed to be the same as steam cracker butenes (45 wt% isobutene and 55 wt% other C_4s). Other chosen conditions are: 98% isobutene conversion, 99.85% MTBE selectivity at a reactor feed mole ratio of 1.1 methanol/ isobutene, and sulfuric acid in the reactor feed of 5 wt% (100% H_2SO_4). The water in the reactor feed is assumed to react completely with isobutene to form tertiary butyl alcohol (TBA). The MTBE product composition and the C_4 product composition are calculated from the composition of streams numbered 18 and 19 at the completion of the material balance calculations.

Reactors. The C_4 feed is mixed with fresh and recycle methanol to give a reactor feed containing 1.1 mole of methanol per mole of isobutene. The reaction mixture is preheated to 70°C and mixed with sulfuric acid recycle. The amount of acid in the reaction mixture is 5 wt%. In the first-stage reactor the reaction mixture is allowed to rise to a maximum temperature of 120°C before cooling is required to control the reaction temperature. In the first reactor, 90% isobutene conversion is achieved and the exit temperature is at 70°C (343°K). The mixture flowrate is 24,942 kg/h and the reactor volume is 54.3 cu m.

TABLE 1—Design basis

MTBE production rate, tpy	100,000
Stream factor	0.90
C_4 feed composition, wt %	
Isobutene	45
Other C_4's	55
Isobutene conversion, %	98
MTBE selectivity, %	99.85
Reactor feed, mol ratio MeOH/isobutene	1.1
Catalyst (100% H_2SO_4)	
in reactor feed, wt %	5
MTBE product composition, wt %	
MTBE	99.0
C_4 hydrocarbons	0.3
Di-isobutene	0.3
Tertiary butanol	0.2
Methanol	0.1
Water	0.08
C_4 product composition, wt %	
C_4 hydrocarbon	96.8
MTBE	1.6
Isobutene	1.6

The reaction mixture is cooled to 40°C and is kept in the range of 40° to 62°C in the second reactor (vol = 54.3 cu m), in which the isobutene conversion of 98% is reached. The exit temperature is 49°C. The material balance around the reactors and subsequent vessels are shown in Table 2.

Settler. From the second-stage reactor the reaction mixture is cooled to 40°C and allowed to separate into an organic phase and an acid phase in the settler. In the settler, 89% of the acid is recovered and recycled. The organic phase is sent to the water washing column. The settler diameter is 2 m and length is 8 m.

Water washing column. A rotating disc contactor is used as a water washing column. The organic phase is washed countercurrently with a water recycle containing sufficient caustic soda to neutralize all the acid, producing sodium sulfate and water. The extract phase containing methanol (15 wt%) is sent to the methanol recovery column and the overhead raffinate phase is fed to the MTBE column. The water washing column is 8-m high and 1-m diameter. There are 14 contacting stages and the column efficiency is 50%.

Methanol column. The methanol-water mixture from the water washing column is preheated to 92°C and distilled in a column packed 6-m high with 25-mm Raschig rings. Open steam is introduced at the bottom of the column. The mole fraction of methanol in the bottoms is 0.005 and in the distillate is 0.980. The recovered methanol is recycled. The bottoms, consisting mainly of water, is recycled and purged. The methanol column is 8-m high and 0.5-m diameter.

MTBE column. The raffinate phase from the water washing column, containing mainly C_4 hydrocarbons and MTBE, is separated in the MTBE column. The feed to the column is preheated to 85°C and distilled to give C_4 mole fraction of 0.990 in the distillate and 0.005 in the bottoms. Both the distillate and bottoms are cooled and stored in